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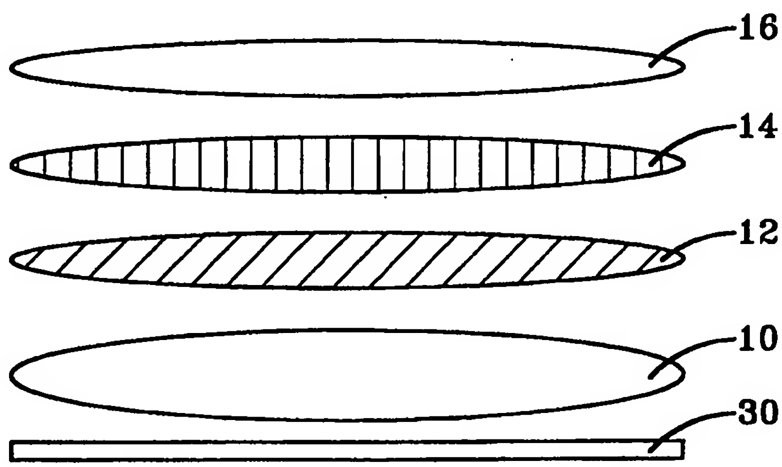
(54) Title: LIMITED USE OPTICAL PLAYBACK DEVICE

(57) Abstract

There is disclsosed a limited use compact disk wherein the number of times the disk can be read is limited. This limited read feature is accomplished through the use of a photochromic material (30) or electrical means (44). The photochromic material (30) or electrical means (44) makes at least a portion of the data contained on the optical disk unreadable or unusable. Methods of manufacturing such limited read CDs are also disclosed.



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LIMITED USE OPTICAL PLAYBACK DEVICE

Technical Field

This invention relates to a limited use optical playback device such as a compact disk. More specifically, the invention relates to the inclusion of a low energy photochromic material in an optically readable device which limits the number of times that information can be obtained from the device. Numerous photochromic materials and methods for the incorporation of the photochromic material in the device are disclosed.

Background

In today's digital world, all types of data are stored in digital form, such as computer software, databases, audio data, and video data. Today, the compact disk (CD) is the storage medium of choice due to its ability to store large amounts of data, exceptional quality, ease of manufacture and long term durability. Since its first release in 1982, there have been more than ten million audio compact disk players sold in the United States and over 1 billion compact disks sold worldwide. Most computers sold today also include a CD-ROM drive (compact disk, Read-Only Memory drive) for software, games and multimedia presentations. "Read-Only" means that one can only view the contents of the CD-ROM; the information on the disk cannot be altered. In contrast, "writeable" or "CD-R's are those disks onto which one can "burn" information in numerous formats. A CD is a medium on which large amounts of information can be stored. Standard CD's can be viewed as a very large, write- protected floppy disk. Presently, CD players are selling at a rate of over 1 million per year, making the CD player the fastest growing consumer electronics product ever introduced.

With the wide spread use of the compact disk as a data storage medium, the compact disk represents an excellent way for marketers and salespersons to advertise their products.

Marketers presently distribute compact disks with software to induce the consumer to enroll in their service (i.e., America On-Line) or to advertise these services or products. However, currently there is no way to limit the use of a compact disk. For example, once a consumer obtains a software compact disk, the consumer may use the software indefinitely or until the compact disk is broken or irreparably damaged. Accordingly, there is a need for a practical way for manufacturers to limit the use of a compact disk, more particularly, to prevent the retrieval of data from a compact disk after a predetermined number of uses. For example, for audio compact disks, it would be advantageous to adapt a compact disk to prevent the user from listening to the audio disk more than one (1) time. Such a limited use compact disk would also allow a consumer to sample a video game before deciding whether to purchase the disk. The limited use feature as described in this invention would prevent the user from using the disk after a predetermined number of times. After sampling the information on the CD, the consumer, if he or she so desired, would then purchase an unlimited play version of the CD from the supplier. Thus among many other advantages, a limited use compact disk would allow marketers the ability to distribute "demo-CD's" to the consuming public for the purpose of marketing new products, computer games, software and musical recordings with assurances that the demonstration disk would be unusable after a predetermined number of uses.

Another embodiment of the limited use CD according to the invention would limit the number of times only a portion or tract of the compact disc data could be retrieved. The advantage of this limited play section of a compact disc becomes obvious when one considers the example of a limited play advertisement added to a music compact disc. The limited play feature of the advertisement is designed to make the advertisement more acceptable to the

audience of the compact disc. The appeal to the advertiser is that by knowing specific likes of the audience of the compact disc, one knowledgeable in the field of advertisement could customize the advertisement to better target those individuals than other means of advertisement. This should dramatically improve the advertisement's effectiveness. The ability to critically target the market is the primary objective of any advertisement. This improved targeting should give this technology a significant preference over other forms of advertisement in the global market that currently spends over $50 billion annually on advertisement.

In its most general form, the limited use compact disk of the present invention comprises a photochromic material deposited upon the disk or a portion of the disk which converts from a relatively transparent form to a relatively opaque form upon contact with the reading radiation. A photochromic material is one which is capable of changing color on exposure to radiant energy.

Much is known about the chemistry and chemical reactions of photochromic materials. It is known, for example, that the photochromic reaction of certain materials can be reversed, i.e., from transparent to colored and vice versa. Many publications and patents have reported the use of photochromic materials to write CD's. In writing a CD, the photochromic material is initially opaque, thus absorbing the writing radiation and is either converted to a transparent form or ablated by thermal energy. However, none of these references have recognized the advantage of using these photochromic materials in the reverse mode. That is, there is no teaching or suggestion that low energy radiation (i.e., typical reading frequencies and energies) could be used to render the data stored on the CD unreadable, by utilizing the reverse chemical reaction of photochromic materials.

Summary of the Invention

It has been discovered here, that data contained on an optically readable device can be rendered unreadable by exposing the colorless state of photochromic materials to low energy radiation sources, e.g., lasers or light emitting diodes, to obtain a colored state thereof. Consequently, there is provided herein a novel optically readable device, e.g., a CD, in which there is provided a substrate having disposed thereon, partially or over its entirety, a film containing a material which is photochromic. The film is changed from its colorless state to its colored state by exposing it to light of appropriate wavelength, e.g., the wavelength of the reading radiation. The reading radiation thus converts the readable CD into a non-readable CD. The photochemical reaction is not easily reversed and thus becomes permanent.

In its broadest sense, the present invention relates to an optically readable device, such as a CD, which comprises a) data contained on said device; and b) means for rendering said data unusable after at least one optical read of said data. The data can be audio, visual, computer programs and the like. The means to render the data unreadable, as further explained below, can be chemical, electrical or a hybred of the two. After one or more reads of the data by the reading radiation, the chemical means, for example, will render the data unreadable or unusable.

Thus, there is disclosed a method of manufacturing a CD adapted for limited number of uses, comprising the steps of providing a transparent substrate, providing pits and lands in the substrate, securing a layer of photosensitive material within the substrate, the photosensitive material being of a predetermined thickness to allow proper focusing of the laser beam of a CD device, the photosensitive material being substantially transparent and adapted to darken upon propagation of the laser beam through the photosensitive material, the

layer of photosensitive material adapted to darken after a predetermined number of plays of the CD so that proper reading of the CD is impeded and securing a layer of reflective coating over the pits and land of the substrate. In an alternative embodiment, the photosensitive material is placed only on a portion or portions of the CD, thus making only selected regions of the CD unreadable after a predetermined number of reads.

There is further disclosed a limited use CD comprising a transparent substrate layer having top and underside portions, the transparent substrate layer having predetermined pits and land portions, a reflective metal layer over the pits and lands of the transparent substrate, a protective layer covering the reflective metal layer and a layer of photosensitive/photochromic material secured to the substrate, the photosensitive/photochromic material is transparent when secured to the CD and adapted to darken upon propagation of light form a light source of a CD device through the photosensitive/photochromic material and wherein the photosensitive/photochromic material darkens to prevent proper reading of the CD.

The photochromic material may be selected from the group consisting of:

(a) an amphipathic derivative of azobenzene, indigo or thioindigo;

(b) silver halide crystals;

(c) spiropyrans and their derivatives;

(d) macrocyclic azaannulene dyes;

(e) polymethine dyes;

(f) anthraquinone dyes;

(g) azulenium dyes;

(h) azo dyes;

(i) methylene blue;

(j) Isol red;

(k) antimony selenium;

(l) tellurium oxide;

(m) fluoride compounds;

(n) at least one element selected from Te, Pb, Au, Sn, As, Bi and carbon, and an iodine compound;

(o) a rhodamine dye;

(p) a J-aggregate;

(q) a H-aggregate;

(r) a metal azide;

(s) a free radical generating compound; and

(t) a liquid crystal.

There is also disclosed a method of making a limited use CD by providing a transparent substrate, providing a first layer of material on the transparent substrate, the first layer of material having portions adapted to reflect light from a light source from a CD device and covering a predetermined portion of the transparent substrate with a photosensitive material transparent when secured to the CD and adapted to darken upon propagation of light from the light source of the CD device through the photosensitive material and wherein the photosensitive material darkens to prevent proper reading of the CD.

In addition to the features mentioned above, objects and advantages of the present invention will be readily apparent upon a reading of the following description.

Brief Description Of The Drawings

Novel features and advantages of the present invention, in addition to those mentioned above, will become apparent to those skilled in the art from a reading of the following detailed description in conjunction with the accompanying drawings wherein similar reference characters refer to similar parts and in which:

Figure 1 is a partial cross section of a conventional compact disk illustrating the layers and components of the disk;

Figure 2 is a graphical depiction of one embodiment of the invention;

Figure 3 is a graphical depiction of a second embodiment of the invention; and

Figure 4 is a block diagram of one embodiment of an electrical circuit that may be used to accomplish the present invention.

Detail Description Of Preferred Embodiment(s)

The preferred system herein described is not intended to be exhaustive or to limit the invention to the precise forms disclosed. They are chosen and described to explain the principles of the invention, and the application of the method to practical uses, so that others skilled in the art may practice the invention.

The present invention may be applied equally to:

1) traditional compact disk technology storing audio data, video data or software;

2) DVD compact disks; and

3) any other equivalent optically readable technology.

The following detailed description describes the limited use compact disk technology of the present invention with respect to traditional audio compact disk standards.

Figure 1 illustrates the layers found in a traditional audio compact disk. A traditional compact disk has a transparent substrate layer (e.g. polycarbonate) **10**, a reflective layer coating (e.g. aluminum) **12** over the substrate **10**, a protective layer **14**, and a label **16**. The compact disks contains "pits" **18** and "lands" **20** in a predetermined pattern in the substrate **10**. The pattern of pits **18** and lands **20** on the compact disk comprise the data contained on the compact disk.

A compact disk contains a long string of pits **18** written helically on the disk. Each pit **18** is approximately 0.5 microns wide and from 0.83 microns to 3.56 microns long. The area between the pits are the areas referred to as lands **20**. As discussed, the pattern of pits **18** and land **20** represent the data of the disk. For audio compact disks the pits and lands represent values of an analog audio signal which may reconstructed by a compact disk player upon reading the digitized information in the form of the pits and lands.

Audio data is converted into digital form to be placed on a compact disk by the steps of:

1) sampling the audio signal at a predetermined rate;
2) quantization of the samples (assigning each sample a discreet value);
3) encoding the data by pulse code modulation (PCM); and
4) transferring the PCM audio data onto a substrate in the form of pits and lands.

The pits **18** and lands **20** are covered by a reflective metal layer **12** such as aluminum. As well understood in the industry, when played, a light source (e.g. a diode laser) from a compact disk device shines on the pits **18** and lands **20**. When the light from the light source strikes a land **20**, the light is reflected back onto a photodetector. When the light strikes a pit **18**, the photodetector will receive no signal or a weak signal. Accordingly, the photodetector

receives a series of light pulses corresponding to the pits **18** and lands **20** in the compact disc. An analog-to-digital converter in the compact disk device converts the series of pulses back into binary coding and then to decimal values. From that data, the analog audio signal can be reconstructed.

The exact specifications and standards of an audio compact disk are found in the "Red Book". The "Red Book" and the other "Books" discussed below are international industry standards that allow CD manufactures to make CD's that can be read on the appropriate CD player. These Books are well known to those in the CD industry. The Red Book describes the physical properties of the audio compact disc and the encoding of the digital audio data. It comprises the following information:

a) audio specification for 16 bit PCM;

b) disc specifications (e.g. transparent substrate having a refraction index of 1.55), including physical parameters (e.g. recording area is 46 mm -117 mm);

c) optical stylus and parameters including laser wavelength (i.e. 780 nm), numerical aperture, pit sizes and track pitch;

d) deviations and block error;

e) modulation system and error correction;

f) subcode channels; and

g) rotational speed (e.g. 1.2-1.4 m/sec).

There is also a Yellow Book for CD-ROM standards, a Green Book for CD-Interactive standards, an Orange Book for recordable CDs, and a Blue Book for Enhanced Music CDs. A set of standards has also been developed for the Digital Versatile Disk or DVD, however, the industry has not formally accepted those standards.

The size of the pits in a CD are very small. Accordingly, the light from the light source should be focused to a very small space on the disk. As the light from the light source enters the substrate **10**, the light bends from entering the substrate which has a refractive index of about 1.55. When the velocity of the light slows, the beam is bent and focusing occurs. The size of the light spot on the disc surface is about 800 micrometers in diameter but is focused to approximately 1 micrometer at the pit surface. The wavelength of the typical CD player laser in air is about 780 nanometers while inside the polycarbonate substrate, having a refractive index of 1.55, the laser's wavelength is about 500 nanometers. In DVD, the laser's wavelength is 650 and 635 nanometers. The shorter wavelengths for DVD are better suited to reading the smaller, more densely packed pits.

The present invention provides a way of configuring the compact disk so that it is limited to a predetermined number of uses. The present invention may be accomplished with various methods and with various compact disk technologies. Again, it is emphasized that although the specification was described with respect to traditional audio compact disk technology, the present invention is not limited to such mediums.

The present invention also provides an electrical method of configuring compact disks, or a section of the disk, so that consumers are limited to a predetermined number of uses. The compact disk is configured so that after a number of readings, an electrical element of the compact disk of the present invention is actuated so as to block/limit penetration of light from the light source. This blockage or disruption of light prevents the compact disk reader or player from properly reading the disk, making the disk useless or the selected sections unreadable. In an additional embodiment, the electrical element alters the control

data encoded on the disk such that the modified control data causes one or more tracks not to be read by the compact reading device.

It is the use of chemical or electrical means to render all or a portion of the data stored on the optically device unreadable, after being read a given number of times, that forms the basis of this invention. This goal is accomplished through the adulteration of at least a critical number of the pits and/or lands to corrupt the data to such an extent that the output is of unacceptable quality. The level of adulteration required to make the output of unacceptable quality will be different for each CD format.

Figures 2 and 3 illustrate graphical depictions of the layers for a compact disk according to two (2) embodiments of the present invention. The compact disk of the present invention (for traditional audio disks) is preferably comprised of: a transparent substrate layer **10** having top and underside portion where the transparent substrate layer **10** has predetermined pits and land portions; a reflective metal layer **12** over the pits **18** and lands **20** of the transparent substrate **10**; a protective layer **14** covering the reflective metal layer **12**; a label **16** over the protective layer and a layer of photochromic material **30** of a thickness, concentration and/or reactivity as determined by the energy and wavelength of the reading radiation and the number of readings permitted. The photochromic material **30** is transparent at first, but is adapted to darken upon propagation of light from the light source of the CD player device through the photochromic material **30** and upon its reflection. It should be understood that the wavelength of the originating light source and its reflection are not the same. This darkening of the photochromic material **30** eventually prevents proper reading of the CD.

Depending on the properties of the material used, the layer of photochromic material **30** may either be secured between the top portion **32** (see **Figure 1**) of the substrate **10** and the reflective metal layer **12** (again for a traditional CD medium) or the layer of photochromic material **30** may be secured to said underside **34** (see **Figure** 1) of the transparent substrate **10**. The photochromic material may also be placed at both locations. An alternative embodiment of the invention resides in the placement of the photochromic material within the substrate **10** during the formulation of the substrate resin layer.

Additionally, the layer of photochromic material **30** may be placed over varying portions of the CD. The material **30** may be placed over the entire surface of the substrate **10**, or merely over selected portions of the surface. For example, the material **30** may be placed over the lead-in portion of the CD, the data portion, or the trailing portion. The portion of the substrate **10** surface to be covered may vary on the cost constraints and the portions of data to be blocked.

The photochromic material **30** used is preferably a photosensitive material that at least partially irreversibly darkens or fatigues upon exposure to the reading radiation of the compact disk player device. It should be understood that the reading radiation includes the initial radiation after impinging upon the reflective layer.

The photochromic material **30** is adapted so that the material **30** will darken after a predetermined number of exposures (exposure time) to the reading radiation. For example, if the photochromic material **30** is placed on the underside **34** of the substrate **10** of a non DVD, the material must be reactive to light with a wavelength of 780 nanometers while it will be reactive at about 500 nanometers if placed on the top side **32** of the substrate **10**.

Accordingly, the CD may only be played a predetermined number of times before the layer of photochromic material **30** darkens to impede proper reading of the CD.

The photochromic material **30** must be adapted to adhere to the substrate **10**, and it must have an appropriate refraction index so as to allow proper focusing of the light source **22** on the desired portion of the CD. Accordingly, if the material is placed on the underside **34** portion of the substrate **10**, it preferred that the refraction index of the material **30** when transparent is close to 1.0.

The Photochromic Material

The basic concept of this invention is that the optically readable medium (i.e., CD) have incorporated into it a material or materials that, upon exposure to the reading wavelength one or more times, will be converted to form that which prevents further effective reading of the disk. Presently, the industry standard for non-DVD CD players is an aluminum gallium arsenide (AlGaAs) semiconductor laser with 0.5 mW power and 780 nm wavelength. As mentioned above, the DVD's will use a laser wavelength of 650 and 635 nm and other different parameters (i.e., track pitch). It should be understood that the basic concept of the invention is not limited to the present standard, however, the detailed description of the invention will be directed to the presently accepted technology.

An additional basic concept of the invention relates to the requirement that the photochromic material, once altered by the reading radiation, substantially remains in its altered state so as to preclude further reading of the optical device. A further concept of the invention relates to the placement of the photochromic material, wherein, in one embodiment, the photochromic material is placed just above the reflective material in the form of a layer or film. In a second embodiment, the photochromic material is placed on the outside of the

substrate, while in a third embodiment, the photochromic material will be dispersed in a continuous or discontinuous manner within the substrate.

The skilled artisan will appreciate that depending upon the refractive index of the substrate, the reading radiation wavelength will change. Thus, if the photochromic material is placed adjacent to the reflective layer, its absorbence spectra should correspond to the wavelength of the reading radiation at that point. In contrast, if the photochromic material is placed on the exterior of the substrate, the maximum absorption spectra of the substrate should be approximately the frequency of the reading laser or diode.

In the most general terms the photochromic material will be photoreactive material that converts from substantially transparent to a form that interferes with the reading radiation to make at least a portion of the data contained on the optical disk unreadable or unusable. At present, a number of commercially available photochemical transformation schemes are known. Photoreactive systems typically, but not always, require an amplification step where a catalyst or an initiator is produced or present for a chemical reaction to occur. It is feasible to induce bond cleavage of the dye, thus transformation, at various frequencies of the electromagnetic spectrum, including the near infrared region.

The photochromic compound can, for example, be based upon the cis-trans isomerization of an amphipathic derivative of azobenzene, indigo or thioindigo having a long chain substituent. The amphipathic compound is preferably in a monomolecular film adjacent the reflective layer of the optical device. More specifically, the azobenzene derivative is 4-monostearoylazobezene, the indigo derivative is N,N'-distearoylindigo and the thioindigo derivative is 5'-octadecyl-5-t-butylthioindigo and/or 5-octadecyl-1,8-naphtylthioindigo.

In one embodiment, the photochromic material is composed in such a way that it has an initial transmittance of at least 40% and an absorbence of at least 20% in the wavelength of the reading radiation at the point of the photochromic materials placement. After exposure to the reading radiation, the photochromic material evidences a decreased transmittance and enhanced absorption of the reading radiation. The level of transmittance and absorbence can be varied to control the number "reads" available to the CD.

In another embodiment, the photochromic material can change reflectance to the reading radiation. Initially, the photochromic material will have reflectance of no more than 20% and after one or more exposures to the reading radiation of at least 40%.

In the situation where the photochromic material is placed in the form of a film or layer, the thickness of the layer can range from 5-400 nm depending upon the number of plays desired and the reactivity of the photochromic material. More specifically, the thickness of the photochromic layer can range from 10-200 nm.

In yet another means of accomplishing the object of this invention, the photochromic material can undergo a phase change to render at least a critical portion of the CD unreadable. More specifically, the reading radiation converts the photochromic or photoreactive material from crystalline to non-crystalline form or vice versa. For example, while in the crystalline form, the photoreactive material allows the metallized layer to reflect the laser light and while in the non-crystalline form, it absorbs or reflects the laser beam thus making the CD, or the portion of the CD in contact with the photochromic material, unreadable.

In any given mode of operation, (i.e., change in absorbence or change in reflectivity), the photoreactive layer will demonstrate durability, reliability and longevity against heat,

humidity and short periods of visible light over a reasonable period of time, say one year, for a limited life CD.

Another means of accomplishing the goal of this invention is to use a thermal deformation technology. In this approach, an initially transparent photoreactive material absorbs the reading radiation and initiates a chemical reaction that generates sufficient heat to deform the pits and lands and/or the substrate to an extent that the recorded data becomes no longer useful. While the energy of the presently available CD player (about 0.5 mW at about 780 nm) is insufficient to cause such deformations, the photoreactive material can be designed such that the reading radiation initiates a chemical reaction of sufficient exothermic energy to render the CD unreadable after a desired number of readings. Photoinitiators and sensitizers known in the art can be used in conjunction with known exothermic reaction components to accomplish the desired result.

One approach to a useful photosensitive material is a photochromic material that has silver halide crystals with dimensions in the range of 50 to 800 angstroms. The silver halide crystals are doped with copper ions and/or another sensitizer selected from mild reducing agents, thioethers, or sulfur-bearing ions which are treated with an agent to accelerate the forward reaction and control the reverse reaction from opaque to transparent. Representative accelerants include ions from the group of cobalt, chromium, manganese, magnesium and rare earth metals such as cerium, samarium and europium. The agent for controlling the reserve reaction is preferably phosphoric acid.

One example of a class of photoreactive or photochromic material that can be altered by a low energy (1 mill watt or less) laser or light emitting diode are the spiropyrans and their derivatives. Typical among these materials is 6' nitro-1,3,3 trimethylindolinobenzospiro-

pyrane; 1,3,3 trimethylindolnapthospiropyran and derivatives such as N-methylacridinonaptho-piropyran, dianthrone, dixanthylene, xanthylideneanthrone and their derivatives.

A light sensitive film forming solution is obtained by preparing a dilute polymer solution (e.g., polymethylmethacrylate) in a solvent compatible with the photochromic material. The so prepared solution is saturated with the photochromic material, so that very thin films having high concentrations of the photochromics can be obtained. A typical film forming solution used in the present invention is prepared by dissolving 240 mg of polymethylmethacrylate in 6 ml of acetonitrile, to which is added 100 mg of 1,3,3 trimethylindolino benzospiropyran. The solution is then coated onto a polymeric substrate by conventional methods, e.g., spinning, dipping, spraying and the like.

The colorless photoreactive layer is then exposed to a 300 nanosecond pulsed laser having a frequency of 780 nm and a power of about 0.5 mw. A series of 3 micrometer spots is obtained thereby. It should be understood that the photochromic material can be chemically modified to absorb and transform a given frequency and energy of a given reading laser light.

Another approach to the goal of the present invention is to include known organic dyes into the transparent substrate to cause the optical transparency of the substrate to change. Exemplary dyes include: macrocyclic azaannulene dyes such as phthalocyanine dyes, naphthalocyanine dyes, porphyrin dyes and the like; polymethine dyes such as cyanine dyes, merocyanine dyes, styryl dyes, squarylium dyes and the like; and further anthraquinone dyes, azulenium dyes, azo dyes and the like. These dyes will absorb the reading radiation and generate heat. As a result, the organic dye melts, vaporizes, sublimes, deforms or changes in

quality the pits and lands, thus rendering them unreadable. This approach is somewhat limited without a thermal initiator as the typical power of the reading radiation is insufficient to cause the needed deformations within two (2) to three (3) reads of the CD.

Yet another approach to accomplishing the objective of this invention is the use of a photo-bleaching photosensitive material. In this embodiment, a section of the disk which encodes reading parameters is covered with an opaque dye, thereby initially preventing the reading of the information by the CD player. After several exposures to the reading radiation, the bleaching of the dye allows the CD player to read the information previously covered. The newly exposed data instructs the CD player to believe that no further information can be obtained from the disk.

Photo-bleaching or photolysis can be accomplished through combining known dyes with various sensitizers or accelerators such as allylthiourea. In the photo-bleaching process, the dye is reduced or oxidized as a result of absorbing radiation. For example, methylene blue, which can be sensitized with reducing agents such as thiosinamide, undergo photoreduction and form colorless leuco-forms, whereas polymethine dyes are oxidized to colorless forms. Certain types of dyes such as Isol Red (available from the Allied Chemical Corp.) are readily photobleachable without an added accelerator. Numerous photobleachable dyes are known in the art and are useful in practicing the invention.

In general, irrespective of the particular methods used to alter spectral absorbence, useful dyes are chosen for their respective compatibilities with binders, for high absorptivity at the wavelength of the respective reading beam and by their ability to render the CD unusable.

Another approach to this invention relates to changes in reflectivity. As a species of photochromic materials, compounds such as antimony selenium (Sb_2Se_3) and tellurium oxide (TeO_x) can be sensitized to the reading frequency to convert from substantially transparent to reflective. Other materials capable of undergoing a change in reflectivity through absorption of reading radiation include fluoride compounds such as BiF_3, MgF_2, PbF_2, LiF, CeF_3, AgF, CaF_2, CrF_2, CrF_3 and carbon fluoride. The film thickness of these compounds can range from 300 Å to 5,000Å. A change in reflectivity can also be accomplished through the use of a film that comprises (a) a substance capable of undergoing an optical change by absorbing the reading radiation such as Te, Pb, Au, Sn, As, Bi and carbon; and (b) a matrix of an iodine compounds, wherein the iodine compound is at least one compound selected from copper iodide, cesium iodide, tin iodide, antimony iodide, zirconium iodide, silver iodide, lead iodide and thalium iodide. Like the opaque approach to the goal of this invention, the increase in reflectivity of the photoreactive layer will render the CD unreadable.

Another example of a useful photoreactive material in the present invention is a rhodamine dye that is dissolved in a non-polar polymer to form a colorless film (leuco form) which, upon exposure to activating light, will become permanently colored without the need for any fixing process. The rhodamine photoreactive materials, as they presently exist, are best suited for reading frequencies of about 2350-3150Å. Chemical modifications to rhodamine dye can shift the effective wavelength to about 800 nm.

The photoreactive material may also comprise at least two (2) types of organic dyes which are, respectively, converted into aggregates by association. As is well known in the art, organic dyes are able to form an aggregate of several dye molecules under certain conditions. In some cases, the aggregate has physical properties, such as stability, spectral

characteristics and the like, completely different from the original dyes. The aggregates useful in this invention include a dimer, a J-aggregate, a H-aggregate and composite materials thereof. J-aggregates are the most preferred. The term "J-aggregate" used herein is intended to mean an aggregate of a plurality of dye molecules without involving any change in chemical structure which has a sharper, visible absorption spectrum range than the component dyes and the absorption spectrum is shifted to longer wavelengths.

The dyes capable of forming J-aggregates include the photochromic dyes. The typical photochromic dyes include spriopyrans, azobenzenes, fulgides, indigoes, thioindigoes, thiarlymethanes and the like. In this invention, the spiropyrams are preferred. J-aggregates are most useful when the reading radiation is in the 500-300 nm range.

A most interesting photoreactive material useful in the present invention is a metal azide. The metal azide acts as an energy amplifying substance. The metal azide used alone or in combination with an energy absorptive dye can be activated by a low energy pulse of laser light and thus disrupt the readability of the CD. For example, the reading radiation initiates the metal azide reaction and the substrate becomes charged or its refractive index is changed. Cupric, lead and silver azides are the best suited since they react highly exothermically and yet can be easily incorporated into the optical device. The metal azide can be applied to the substrate in a binder of polymeric material, such as gelatin or applied directly by vapor deposition. The layer of photosensitive material will typically be 0.5 to 5 microns thick. Erythrosin, erythrosin B, sudan III, rhodamine 6G and rose bengal dyes are all suitable for use with the metal azide.

Technology developed for the laser printer industry is also applicable in this invention. For example, the substrate may have coated upon it a heat sensitive, color-

developing layer containing a basic dye and an organic developer. A second layer containing a near infrared absorbent (optionally including a metal azide) is then placed adjacent the color layer. The reading radiation causes the generation of heat by the absorbent layer which in turn causes the color-developing layer to be activated.

In yet another approach to the invention, the photoreactive material may comprise a free radical generating compound. The free radical generating compound may be activated directly by the reading radiation or as the result of heat generated by an absorptive dye. The free radicals thus generated, can go on to promote any number of reactions to result in the CD becoming unreadable (i.e., bleaching). More specifically, the free radical generating compound can be selected from azo compounds, diacryl peroxides, dialkyl peroxides, hydroperoxides, sulfur compounds, carbonyl compounds, halogen compounds, reducing dyes, organometallic compounds and persulfates.

Another interesting means of producing a limited read CD involves the use of liquid crystals. In this embodiment, the photoreactive layer comprises at least one type of liquid crystal that is capable of changing states, such as agglomeration or arrangement, upon absorption of the reading radiation. The liquid crystal may also be combined with radiation absorbing dyes to promote the change in radiation transmission.

It is known that polymer dispersed liquid crystals (PDLCs) can be used to moderate infrared light. This approach would also be useful in the present invention. A wide range of polymers can be used to hold the liquid crystal, for example, polyvinylpyrrolidone (PVP). PDLCs are made by dispersing the nematic material E7 in the PVP polymer binder. The PDLC is then placed between two substrates and integrated into the CD.

Another approach to the invention relates to a photochromic material containing a copolymer of a spirobenzothiopyran derivative prepolymer and a liquid crystal prepolymer. The spirobenzothiopyran prepolymer is typically used in a quantity of 1-50 parts by weight based on 100 parts by weight of the liquid crystal prepolymer.

The photoreactive material according to the invention may also be a liquid crystalline high polymer having side chains and a dyestuff having a reading light absorbing property. The liquid crystal polymer has side chain groups provided with molecular rotation power or power of changing state such as an agglomeration or an arrangement. Upon radiation of this material by the reading laser, affinity and association between the polymer compound and the dye compound are induced or disassociation and separation of the dye compound from the polymer compound are induced due to differences in chemical and physical characteristics such as glass transition point. This mechanism changes the optical property from substantially transparent to opaque.

Manufacturing Techniques

There are several main considerations when manufacturing optical devices according to the invention. The first is accuracy. A supplier of limited read CD's must be assured that the precious data becomes unusable after a given number of reads Depending upon the given approach and photoreactive material chosen, one skilled in the art can readily determine the exact parameters (i.e., film thickness, sensitivity and the like) required to accomplish the desired number of reads before the disk becomes unusable. The second major concern is speed of manufacture. Given the fact that the CD's according to this invention will be distributed free of charge, the costs to produce them must be minimized. This requires a high speed assembly line type process. In addition, the system must be able to shift rapidly from

the production of one disk to the production of another, due to the large number of artists and software and the rapidly shifting nature of the modern consumer's tastes. This means that most of the equipment for the manufacturing process be common to every conceivable CD produced. One invaluable aspect of the invention resides in the ability to produce limited read CD's without the use of expensive, inefficient and exotic manufacturing processes.

The present invention can be accommodated into any of the known processes for manufacturing CD's, such as the standard stamper-injection molding technique, the direct read and write mastering techniques, the direct metal mastering technique, photopolymerization, glass mastering and the like.

When the photoreactive material is placed adjacent to the reflective layer or on the top surface of the substrate, a spin-coating method is generally preferred for easy film formation and economy. In this approach, the photoreactive/photochromic material or photoreactive system is dissolved in an appropriate solvent that will not adversely affect the substrate employed or the photochromic material. In the case of a polycarbonate substrate, exemplary, suitable solvents include; aliphatic or alicyclic hydrocarbons such as hexane, heptane, octane, cyclohexane and the like; non-polar ether solvents such as diethyl ether, dibutyl ether and the like; polar alcohol solvents such as methyl alcohol, ethyl alcohol, allyl alcohol, cellosolve and the like. The photosensitive material/solvent mixture may also include binders such as resins and gelatin.

The photoreactive material can also be applied to CD structure by means of dip-coating, spray-coating, roll-coating and the like.

In an alternative embodiment, the photosensitive material is dispersed within the substrate. In this approach, the photosensitized material may or may not be copolymerized

with the substrate resin. While eliminating the need for an additional coating step (i.e., spin coating), the incorporation of the photosensitive material into the substrate resin will require careful attention to processing parameters such as thermal degradation of the photosensitive material and manufacturing techniques.

Electrical Method

In another embodiment of the present invention, an electric circuit may be used to detect the reading radiation and to initiate a process of rendering a predetermined portion of the CD unreadable. **Figure 4** illustrates an example block diagram of one embodiment of an electrical circuit that may be used to accomplish the functions of the present invention.

Due to present day fabrication techniques, the small circuit of **Figure 4** may be fabricated on a very small chip that may be bonded to the CD substrate. In a preferred embodiment, the circuit is bonded to the polycarbonate substrate surface. The circuit should be bonded so that its placement will not block exposure of the laser to the information bearing pits and lands of the CD (e.g., outside or inside the recording area). Although the circuit should be placed so as not to interfere with the playing of the CD, the photodiode should be placed on the substrate in a location that will enable it to detect the reading radiation from the CD laser upon each play of the CD.

In the embodiment of **Figure 4,** a photodiode **40** detects the radiation from the laser as reading of the CD is initiated. The photodiode **40** detects the radiation from the laser and converts the energy into an electrical signal. The photodiode **40** is adapted to detect the output of the standard laser, the specifications of which were discussed above, This electrical signal is preferably amplified and fed into an input of a counter circuit **42**. The counter **42,** initially set to zero values, keeps track of the number of times the CD is read (i.e., played).

After a predetermined count (i.e., CD plays), the counter **42** outputs are used to initiate a means for interfering with the reading radiation **44** to make at least a portion of the data contained on the optical disk unreadable or unusable. For example, a predetermined number of the counter **42** outputs may be connected to the inputs of an AND gate **46**, the output of which is used to initiate the means for interfering with the reading radiation **44.**

The means for interfering with the reading radiation **44** of the CD light may be a liquid crystal layer sandwiched between the other layers of the CD. The liquid crystal layer will switch from a transparent light to a light scattering state upon the application of an electric field (e.g. when initiated by the counter **42** of **Figure 4,** for example). In an ON state, the light from the reading laser is scattered by the orientation of the liquid crystals (i.e., the liquid crystals are opaque). In the OFF state (i.e., electric field is applied) the liquid crystals are reoriented along the field causing the liquid crystal to transmit light. Orientation of the liquid crystals within the substrate are directed according to well known principles. Transparent electrodes as known in the art may be used to conduct electric signals to the liquid crystals without interfering with the reading light. In another embodiment, the means for interfering with the reading radiation **44** of the laser is a predetermined transparent chemical layer, preferably deposited on the polycarbonate substrate layer, that turns opaque when stimulated by an electrical signal. In the preferred embodiment, the circuit of **Figure 4** is powered by a battery **50**. In another embodiment, the means for the interfering with the reading radiation of the laser will be a light source of about 500 nm located on the circuit.

Industrial Applicability

The software and entertainment industries are constantly searching for techniques to promote their products to the consumer. While the "free sample" approach is convenient for soap and detergent suppliers, it has failed to gain acceptance in the CD industry. This invention now provides a means for the software and video game industry to allow consumers to sample their wares a limited number of times to induce the purchase of a fully useable version.

Having shown and described a preferred embodiment of the invention, those skilled in the art will realize that many variations and modifications may be made to affect the described invention and still be within the spirit of the claimed invention. Thus, many of the elements indicated above may be altered or replaced by different elements which will provide the same result and fall within the scope of the claimed invention. It is the intention, therefore, to limit the invention only as indicated by the scope of the claims.

WHAT IS CLAIMED IS:

1. An optically readable device comprising:

a) data contained on said device; and

b) means for rendering said data unusable after at least one optical read of said data.

2. A method of manufacturing a compact disk (CD) adapted for limited number of uses, comprising the steps of:

(a) providing a transparent substrate;

(b) providing pits and lands in said substrate;

(c) securing a layer of photochromic material to a predetermined portion of said substrate, said photochromic material being of a predetermined thickness to allow proper focusing of the laser beam of a CD device, said photochromic material being initially substantially transparent and adapted to become less transparent upon propagation of said laser beam through said photochromic material, said layer of photochromic material adapted to render a critical percentage of the data contained on said CD unreadable after a predetermined number of plays; and

(d) securing a layer of reflective coating over said pits and land of said substrate.

3. The method according to claim 2 wherein said layer of photochromic material is secured to the underside portion of said substrate.

4. The method according to claim 2 wherein said layer of photochromic material is placed over a lead-in portion of said CD.

5. The method according to claim 2 wherein said layer of photochromic material is placed substantially over a data storage portion of said CD.

6. The method according to claim 2 wherein said photochromic material is selected from the group consisting of:

(a) an amphipathic derivative of azobenzene, indigo or thioindigo;

(b) silver halide crystals;

(c) spiropyrans and their derivatives;

(d) macrocyclic azaannulene dyes;

(e) polymethine dyes;

(f) anthraquinone dyes;

(g) azulenium dyes;

(h) azo dyes;

(i) methylene blue;

(j) Isol red;

(k) antimony selenium;

(l) tellurium oxide;

(m) fluoride compounds;

(n) at least one element selected from Te, Pb, Au, Sn, As, Bi and carbon, and an iodine compound;

(o) a rhodamine dye;

(p) a J-aggregate;

(q) a H-aggregate;

(r) a metal azide;

(s) a free radical generating compound; and

(t) a liquid crystal.

7. The method according to claim 6 wherein said photochromic material comprises a compound selected from the group consisting of 4-monostearoylazobenzene, N,N'-distearoylindigo, 5-octadecyl-5'-t-butylthioindigo, 5-octadecyl-1,8-naphtylthioindigo, 6' nitro-1,3,3 trimethylindolinobenzosprio-pyrane, 1,3,3 trimethylindolnapthospriopyran, phthalocyanine dyes, naphthalocyaine dyes, prophyrin dyes, cyanine dyes, mecrocyanine dyes, styryl dyes, squarylium dyes, anthraquinone dyes, azo dyes, BiF_3, MgF_2, PbF_2, LiF, CeF_3, AgF, CaF_2, CrF_2, CrF_3, carbon fluoride, erythrosin, erythrosin B, sudan III, rose bengal and peroxides.

8. The method according to claim 2 wherein said layer of photochromic material is placed over a lead-out portion of said CD.

9. The method according to claim 2 wherein said photochromic material becomes less transparent upon irradiation at a wavelength of about 780 nm.

10. A CD made in accordance with the process of claim 2.

11. A method of making a limited use compact disk (CD), said CD comprised of a transparent substrate, comprising the steps of:

(a) providing a CD; and

(b) securing a photochromic material over a predetermined portion of said transparent substrate, said photochromic material being substantially transparent prior to exposure to reading radiation.

12. The method according to claim 10, wherein said photochromic material is selected from the group consisting of:

(a) an amphipathic derivative of azobenzene, indigo or thioindigo;

(b) silver halide crystals;

(c) spiropyrans and their derivatives;

(d) macrocyclic azaannulene dyes;

(e) polymethine dyes;

(f) anthraquinone dyes;

(g) azulenium dyes;

(h) azo dyes;

(i) methylene blue;

(j) Isol red;

(k) antimony selenium;

(l) tellurium oxide;

(m) fluoride compounds;

(n) at least one element selected from Te, Pb, Au, Sn, As, Bi and carbon, and an iodine compound;

(o) a rhodamine dye;

(p) a J-aggregate;

(q) a H-aggregate;

(r) a metal azide;

(s) a free radical generating compound; and

(t) a liquid crystal.

13. The method according to claim 12, wherein said photochromic material comprises 4-monostearoylazobenzene, N,N'-distearoylindigo, 5-octadecyl-5'-t-butylthioindigo, 5-

octadecyl-1,8-naphtylthioindigo, 6' nitro-1,3,3 trimethylindolinobenzosprio-pyrane, 1,3,3 trimethylindolnapthospriopyran, phthalocyanine dyes, naphthalocyaine dyes, prophyrin dyes, cyanine dyes, mecrocyanine dyes, styryl dyes, squarylium dyes, anthraquinone dyes, azo dyes, BiF_3, MgF_2, PbF_2, LiF, CeF_3, AgF, CaF_2, CrF_2, CrF_3, carbon fluoride, erythrosin, erythrosin B, sudan III, rose bengal and peroxides.

14. The method according to claim 11 wherein said layer of photochromic material is placed over a lead-out portion of said CD.

15. The method according to claim 11, wherein said photochromic material is placed on an underside portion of said substrate.

16. A CD made in accordance with the process of claim 11

17. A limited use CD comprising:

(a) a transparent substrate layer having top and underside portion, said transparent substrate layer having predetermined pits and land portions;

(b) a reflective metal layer over said pits and lands of said transparent substrate;

(c) a protective layer covering said reflective metal layer;

(d) a layer of photochromic material secured to said substrate, said predetermined material transparent when secured to said CD and adapted to darken upon propagation of light from a light source of a CD device through said predetermined material, and wherein said predetermined material darkens to prevent proper reading of said CD.

18. A limited use CD according to claim 17, wherein said layer of photochromic material is secured between said top portion of said substrate and said reflective metal layer.

19. A limited use CD according to claim 17, wherein said layer of predetermined material is secured to said underside of said transparent substrate.

20. A limited use CD according to claim 17, wherein said CD is an audio disk formatted according to the Red Book.

21. A limited use CD according to claim 17, wherein said reflective metal layer selected from aluminum, silver and gold.

22. A limited use CD according to claim 17, wherein said layer of photochromic material is selected from the group consisting of:

(a) an amphipathic derivative of azobenzene, indigo or thioindigo;

(b) silver halide crystals;

(c) spiropyrans and their derivatives;

(d) macrocyclic azaannulene dyes;

(e) polymethine dyes;

(f) anthraquinone dyes;

(g) azulenium dyes;

(h) azo dyes;

(i) methylene blue;

(j) Isol red;

(k) antimony selenium;

(l) tellurium oxide;

(m) fluoride compounds;

(n) at least one element selected from Te, Pb, Au, Sn, As, Bi and carbon, and an iodine compound;

(o) a rhodamine dye;

(p) a J-aggregate;

(q) a H-aggregate;

(r) a metal azide;

(s) a free radical generating compound; and

(t) a liquid crystal.

23. A method of making a limited use compact disk:

(a) providing a transparent substrate;

(b) providing a first layer of material on said transparent substrate, said first layer of material having portions adapted to reflect light from a light source from a compact disk device;

(c) covering a predetermined portion of transparent substrate with a photochromic material substantially transparent when secured to said compact disk and adapted to darken upon propagation of light from said light source of said compact disk device through said photochromic material, and wherein said photochromic material darkens to prevent proper reading of said compact disk.

24. The method according to claim 23, wherein said first layer of material is a reflective metal layer.

25. The method according to claim 23, wherein said first layer of material is a organic dye.

26. The method according to claim 23, wherein said compact disk is a DVD disk.

27. The method according to claim 26 wherein said photochomic material becomes less transparent upon evidiation at a wavelenght of about 635 nm.

28. The method according to claim 26 wherein said photochromic material becomes less transparent upon inadiation at a wavelength of about 650 nm.

29. A limited use CD comprising:

(a) a CD having a transparent substrate layer;

(b) an electrical circuit for detecting reading radiation from a CD player, said electrical circuit bonded to a predetermined portion of the CD, said electrical circuit comprising:

(i) a photo diode for detecting said reading radiation;

(ii) a counter circuit in electrical communication with said photodiode, said counter circuit being incremented upon said reading radiation being detected by said photo diode;

(iii) a means for interfering with said reading radiation, said means for interfering with said reading radiation being activated when said counter reaches a predetermined value.

30. A limited use CD according to claim 29, wherein said means for interfering with said reading radiation is a liquid crystal layer adjacent said transparent substrate layer, said liquid crystal layer connected to electrodes, said liquid crystal layer blocking said reading radiation when an electrical field is applied to said electrodes upon said counter reaching said predetermined value.

31. A limited use CD according to claim 29, wherein said means for interfering with said reading radiation is a light source of about 500 nm, said light source connected to electrodes, said light source interfering with said reading radiation when an electrical

field is applied to said electrodes upon said counter reaching said predetermined value.

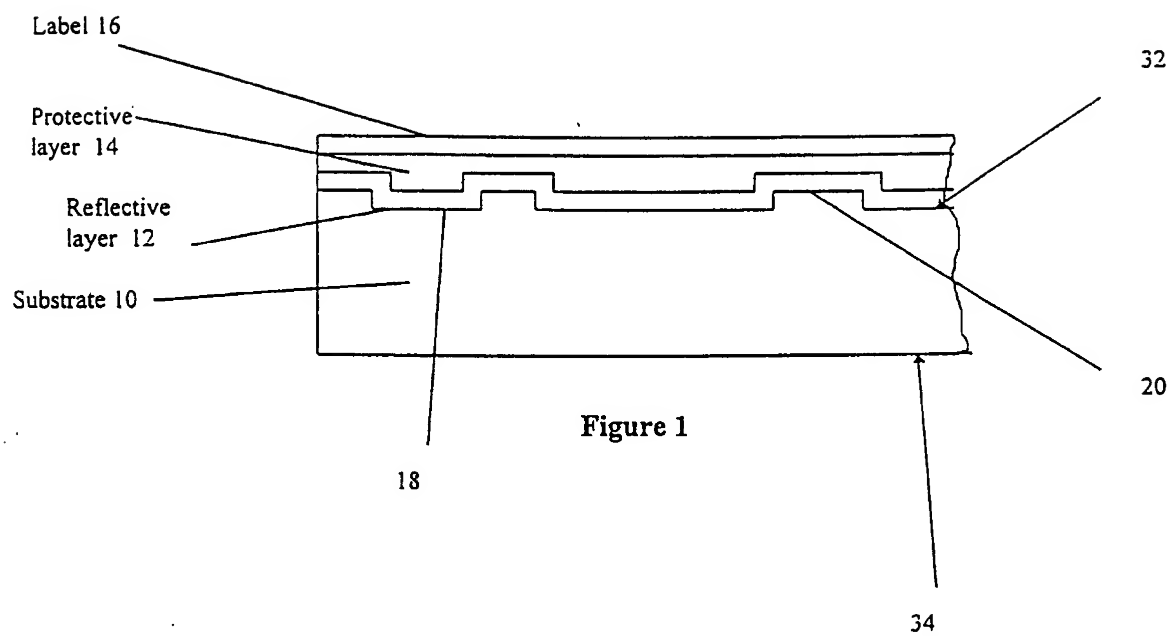
Label 16
Protective layer 14
Reflective layer 12
Substrate 10
32
20
18
34

Figure 1

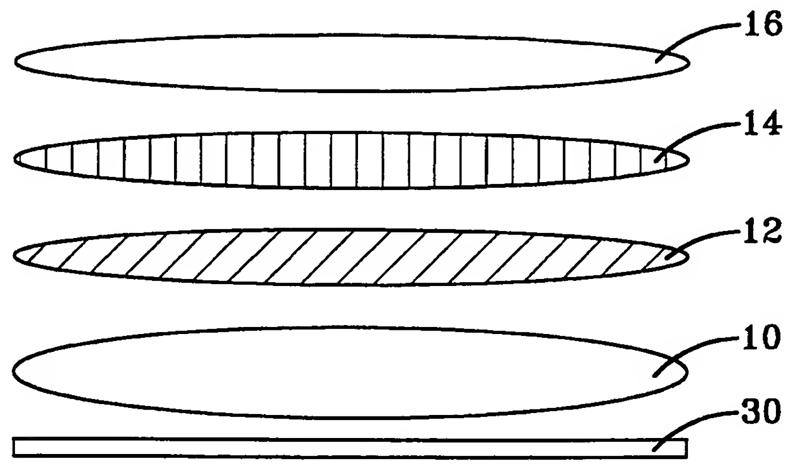

FIG-2

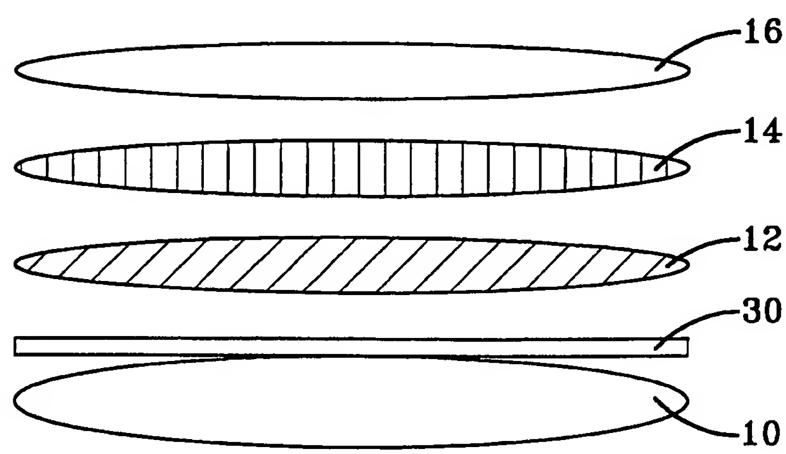

FIG-3

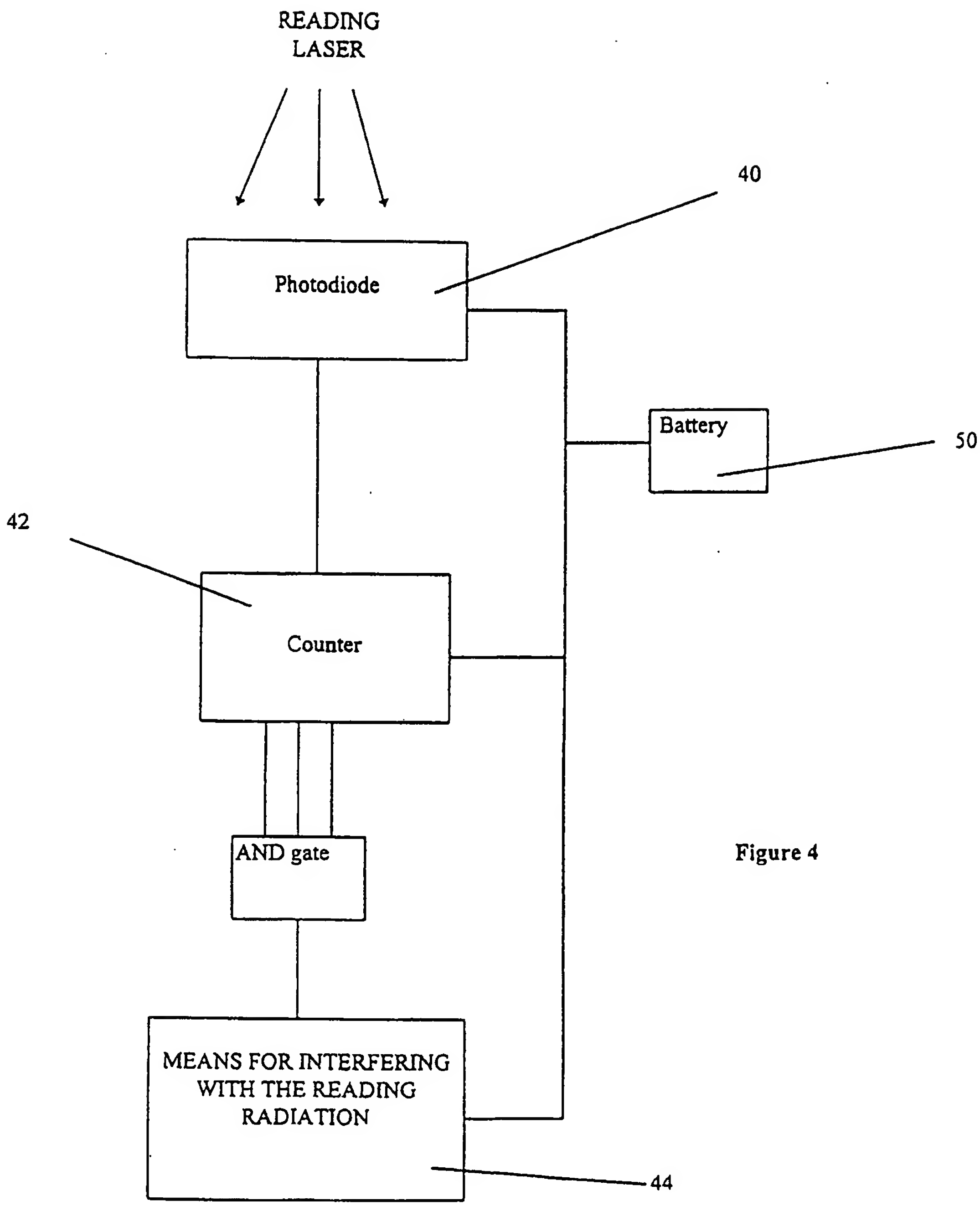
READING
LASER
40
Photodiode
Battery
50
42
Counter
AND gate
MEANS FOR INTERFERING
WITH THE READING
RADIATION
44

Figure 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/02406

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : G11B 3/90, 7/00, 3/70; G03F 9/00; G03C 1/492
US CL : 369/54, 100, 284; 430/4, 270.11
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 369/53, 54, 100, 272, 283, 284; 430/4, 20, 269, 270.1, 270.11

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	US 5,815,484 A (SMITH et al) 29 September 1998, col. 8, lines 4-14.	1-28
A	US 5,513,260 A (RYAN) 30 April 1996, entire document.	1-31
A	US 5,453,968 A (VELDHUIS et al) 26 September 1995, entire document.	1-31

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
08 APRIL 1999	07 MAY 1999

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	PAUL W. HUBER Joni Hill Telephone No. (703) 305-3900

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/02406

B. FIELDS SEARCHED
Electronic data bases consulted (Name of data base and where practicable terms used):

APS
search terms: copy(10a)protect?, photochromic, prevent(20a)(read? or reprod?)